Electrochemical behavior of hafnium in (NaCl–KCl–NaF–HfO₂) molten salt

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Abstract. The electrochemical reaction mechanism and electro crystallization process of hafnium in the NaCl-KCl-NaF-HfO₂ molten salt were examined at 973K by means of cyclic voltammetry, chronopotentiometry, and chronoamperometry techniques. The results show that the electrochemical reduction mechanism of hafnium in the NaCl-KCl-NaF-HfO₂ molten salt system is $\text{Hf}^{4+} + 4\text{e}^- \rightarrow \text{Hf}$. The electro crystallization process of hafnium is found to be an instantaneous hemispheroid three-dimensional nucleation process and the hafnium ion diffusion coefficient of $4.744 \times 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1}$ is tested in this study.

Introduction

Hafnium is of considerable interests and practical importance due to its unique properties in technological applications. Since the 1950s, the preparation of metal hafnium with a very high melting point (2503K) have become a hot research around the world [1-5]. Hafnium is being intensively studied for a number of potential applications, e.g., getter, bulb and electronic valve [6-8]. In the nuclear power industry, hafnium is often employed as control rods for nuclear reactors [9-11] to control the amount of thermal neutrons, especially in water-cooling high power and long life heap [12]. Hafnium and its alloys also display outstanding corrosion resistance. A variety of methods have been used to prepare metal hafnium film, however, electrodeposition is one of the important techniques because of its low cost.

Sharma et al [13] studied the preparation of metal hafnium by reducing hafnium dioxide from calcium. The preparation by aluminothermic reduction hafnium dioxide have been reported by Gosse and Albert [14]. Gosse et al [15] studied the preparation of metal hafnium by reducing hafnium dioxide with Silicon and carbon, but so far, these attempts were unsuccessful. Fray et al [16] reported the preparation of metal for the first time using metallic oxide based on the molten salt electrolysis method. Heating reduction with magnesium was studied in detail by Ye Z G [17], the research focuses on electrolytic refining of hafnium sponge. However, it pollutes environment because of products of chlorine in actual production process, so it is not suitable for mass production. However, all the research paid attention to the thermal reduction, and very limited research has been carried out on electrochemical reaction process and particularly on molten salt.

At present, owing to fewer reports of the electrochemical reduction mechanism of metal hafnium, it is still unclear what the electrochemical reduction mechanism of electrodeposition of metal hafnium in molten salts and electrocrystallization process are. But in this paper, it will introduce a new system of molten salt: NaCl-KCl-NaF-HfO₂, and study the mechanism of electrochemical reduction of hafnium in the molten salt system by cyclic voltammetry and chronopotentiometry and its electric crystallization process by chronoamperometry, which will provide a theoretical basis for preparing hafnium by electrolysis process.

Experiments

Pretreatment of Reagents. All the reagents in the experiments were analytic reagents. The mixture of $\text{NaCl}:\text{KCl}:\text{NaF}:\text{HfO}_2=0.35:0.35:0.3:0.03$ in molar ratio was dried under a Electrothermal Constant-temperature Dry Box for more than 8h at 473K to remove residual water thoroughly and then grinded in an agate mortar for experiments.

Electrode selection and preparations. A three-electrode cell was used for the electrochemical experiments. The platinum wire was selected as the working electrode; the graphite crucible was served as an auxiliary electrode; the high pure metal platinum was selected as the reference electrode. All electrodes surfaces were processed before experiment to obtain exact experimental results, two platinum wire were mainly processed in this experiment. The electrodes surfaces of two platinum wire were sandpapered in the first place, then polished and cleaned with alcohol, finally the platinum wire were washed carefully in deionized water.

Experimental facility. The temperature of the resistance furnace was controlled by an artificial intellectual controller (Model:AI-808p) and temperature measurements were carried out by the platinum-platinum rhodium thermocouple (Model:S) with an accuracy of $\pm 1^\circ\text{C}$. The electrochemical reduction mechanism and electrocrystallization process of hafnium in $\text{NaCl-KCl-NaF-HfO}_2$ system were performed in electrochemical measurement workstation (Model: IM6eX, Germany).

Experimental process. All electrochemical experiments were carried out in a sealed stainless-steel container under dry argon atmosphere. The electrolytic crucible was made of high purity graphite, positioned in the stainless steel outer vessel, then heated from the room temperature to the working temperature of 973K. Keep the temperature at 973K for 4h and make the dissolution of hafnium dioxide in the $\text{NaCl-KCl-NaF-HfO}_2$ molten salt system reach saturation. Then the working electrode and reference electrode were put into the electrolytes for testing in the electrochemical measurement workstation.

Electrochemical reduction mechanism of hafnium

Cyclic voltammetry. Figure 1 shows the voltammograms of the hafnium electrode in the $\text{NaCl-KCl-NaF-HfO}_2(x\text{NaCl}:x\text{KCl}:x\text{NaF}:x\text{HfO}_2=0.35:0.35:0.3:0.03)$ system at 973K.

In the voltammograms, reduction peak a and oxidation peak b in the $\text{NaCl-KCl-NaF-HfO}_2$ molten salt system were observed at 973K. The reduction peak in the molten salt system was all appeared in different scanning rates. The correlation data obtained from Fig. 1 are shown in Table 1.

The study of the voltammetric curves (Fig.1; Table1) recording different potential scanning rates clearly shows that the values of E_{pc} and E_{pa} are unrelated to the potential scanning rates. Electric current function ($ipc/v^{1/2}$) is related to the scanning rate v and they show a strict linear relation (Fig.2). According to the above analysis, it is seen that hafnium ion in the $\text{NaCl-KCl-NaF-HfO}_2$ molten salt system is a reversible process, meaning that the electrochemical reaction process of hafnium in this system is controlled by ion diffusion rate.

Fig. 1 Cyclic voltammograms at various potential scan rates in $\text{NaCl-KCl-NaF-HfO}_2$ system at 973K

Table1 Major parameters in cyclic voltammetry curve of the molten salt

No.	$v/\text{mV}\cdot\text{s}^{-1}$	I_{pc}/A	$i_{pc}/\text{A}\cdot\text{cm}^{-2}$	E_{pc}/V	$E_{pc/2}/\text{V}$	$E_{pc}-E_{pc/2}$	$i_{pc}/v^{1/2}$
1	600	-0.07136	-0.22575	-0.87	-0.855	-0.015	-0.00922
2	500	-0.06302	-0.19937	-0.883	-0.867	-0.016	-0.00892
3	400	-0.05166	-0.16343	-0.879	-0.862	-0.017	-0.00817
4	300	-0.04371	-0.13828	-0.843	-0.827	-0.016	-0.00798

Fig.2 Relationship between i_{pc} and $v^{1/2}$ from Table 1

The mixture were taken into the high purity graphite in the same molar ratio, keep the temperature at 973K for 4h. The low-Carbon Steel was selected as the cathode and the high purity graphite was selected as the anode. Constant potential electrolysis on cathode was carried out at 0.87V for 30 min. It is found that black film material on the cathode is hafnium which is proved by EDS (Fig.3). After quenching, the NaCl-KCl-NaF-HfO₂ molten salt for the experiment was characterized by X-ray diffraction (XRD). Figure 4 shows that the main existence form of hafnium ion in the system, which is reduced to metallic hafnium.

Since the values of E_{pc} have a little change with the increase of scanning rate v (Table1). For reversible process but unsolvable product, the relationship of E_{pc} , $E_{pc/2}$, and electron number n can be expressed as follows[18]:

$$E_{pc}-E_{pc/2}=-0.77(RT/nF) \quad (1)$$

where n , F , R , T are, respectively, reacting electron number, Faraday constant, gas constant, and the experiment temperature (973K).

Fig.3 EDS diagram of cathode product at the peak of cathode potential

Fig. 4 XRD pattern of NaCl-KCl-NaF-HfO₂ molten salt system

Introducing the experiment data $E_{pc}-E_{pc}/2$ (Table 1) to Eq.(1), the reacting electron number at reduction peak in Fig.1 can be 4. The electrochemical reaction process of hafnium is $Hf^{4+}+4e \rightarrow Hf$, so the system is a reversible process transferring 4 electrons in one step and the product cannot be dissolved.

Chronopotentiometry. The NaCl-KCl-NaF-HfO₂ molten salt system was investigated at 973K (700°C) by chronopotentiometry. When a sudden constant current (0.25mA) applied to the system in 3 seconds, the changes of the electrode potential over time was recorded in Fig.5. When a sudden constant current applied to the system, The electrode potential will have great changes because of the ohmic polarization of the solution on the electrode surface, as shown on curve o-a. As a result of hafnium deposited on the cathode under a constant current polarization, the electrode potential increases to the characteristic value of this reduction reaction, as shown on curve a-b. With the reduction of electrical activity hafnium ion and the precipitation of hafnium on the cathode, the concentration ratio of matters in oxidation state to matters in reduction state changes continuously with the electrolysis time. When the concentration ratio close to 1, the electric potential changes slowly, as shown on curve b-c in Fig.5. When the diffusion rate of electrical activity hafnium ion on the electrode surface is not as fast as the electrode reaction rate, the concentration polarization is caused and increases greatly the electrode potential as shown on curve c-d in Fig.5. When the concentration of hafnium ion on the electrode surface decreases to zero (corresponding to location d in Fig.5), the electric potential changed rapidly and it indicates a new ion electrochemical reduction process to occur on the electrode.

Fig. 5 Chronopotentiometry curve of NaCl-KCl-NaF-HfO₂ molten salt system

According to Sand equation[18-19], the relation between the transition time τ and the diffusion coefficient D of electrical activity ion in the solution can be derived by:

$$D = \frac{t \cdot 2^2 \cdot i^2}{n^2 \cdot F^2 \cdot p \cdot C^2} \quad (2)$$

where C is the concentration of HfO_2 .

Table 2 Data from chronopotentiometry curve of NaCl–KCl–NaF–HfO₂ molten salt system

I/A	$i/\text{A} \cdot \text{cm}^{-2}$	τ/s	$D/\text{cm}^2 \cdot \text{s}^{-1}$	$\bar{D}/\text{cm}^2 \cdot \text{s}^{-1}$
0.25	1.053	1.809	3.808×10^{-4}	
0.3	1.2631	1.640	4.967×10^{-4}	4.744×10^{-4}
0.35	1.4737	1.324	5.458×10^{-4}	

Taking the chronopotentiometry curve of $I=350\text{mA}$ as an example, Table 2 lists a part of data extracted from Fig.5 and diffusion coefficient D of electrical activity hafnium ion figured out by Eq.(2). The diffusion coefficient of hafnium ion in the system is $4.744 \times 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1}$. Regardless of the electrode process is reversible or irreversible, E and $\ln(\tau^{1/2} - t^{1/2})$ are linear relation, and the slope is different. When E and $\ln(\tau^{1/2} - t^{1/2})$ are linear relation, the electrode process is reversible and the product is insoluble. Fig.6 shows that the electrode process of hafnium in the NaCl–KCl–NaF–HfO₂ system is a reversible process and the product is insoluble, the reacting electron number can be 4, which is the same as that measured by cyclic voltammetry.

Fig. 6 Relationship between E and $\ln(\tau^{1/2} - t^{1/2})$ from chronopotentiometry curve

Electrocrystallization process of hafnium. The electrocrystallization process of hafnium was investigated by using chronoamperometry at 973K in the NaCl–KCl–NaF–HfO₂ molten salt system(Fig.7). Each curve shows the typical diffusion-controlled process of ion, and the change of current–time transient curves indicates the electrocrystallization nucleation characteristics of hafnium on the cathode. At the beginning, the double layer of hafnium electrode is charged and the first nuclei of hafnium are formed, so the current increases to a high value in a very short time. Subsequently, the current decreases because of concentration polarization, which is the result that the number of hafnium ion electro-migrated to the active position could not meet the nucleation rate of hafnium. Then, owing to the growth of hafnium crystal nucleuses formed on the cathode and the deficiency of active ion in the diffusion layer, the current decreases slowly and drives to stabilization.

Fig. 7 Chronoamperometry curves of NaCl-KCl-NaF-HfO2 molten salt system

Taking curve (b) in Fig. 7 as an example, data of current I and time t from curve (b) are presented in Table 3. Curves of I - $t^{1/2}$ and I - $t^{3/2}$ are shown in Fig.8. By using the data from Fig.8, the following linear regression Eqs. (3) and (4) are obtained. R^2 of Eq. (3) is 0.97216, which means existing linear relation between I and $t^{1/2}$. R^2 of Eq. (4) is 0.90236, which means there is no linear relation between I and $t^{3/2}$.

$$I = 0.20831 - 0.09699t^{1/2} \quad R^2 = 0.97216 \quad (3)$$

$$I = 0.08126 - 0.00838t^{3/2} \quad R^2 = 0.90236 \quad (4)$$

Table3 Data of current I and time t from curve (b) of chronoamperometry curves in Fig.7

t / s	I / A	$t^{1/2} / s^{1/2}$	$t^{3/2} / s^{3/2}$
3.35	0.03119	1.8303	6.1315
3.45	0.0282	1.8574	6.4081
3.55	0.02495	1.8841	6.6887
3.65	0.02246	1.9105	6.9733
3.75	0.0212	1.9365	7.2618

Fig. 8 Curves of a I - $t^{1/2}$ and b I - $t^{3/2}$ of curve (b) in Fig. 7

According to hemispheroid three-dimensional nucleation theory[20], when the electrocrystallization process is controlled by diffusion of metallic atom on electrode surface and is progressive nucleation growth, the relation of I to t is represented by Eq. (5):

$$i = \frac{2}{3} z F p K_n N \left(\frac{M}{r} \right)^{1/2} (2C_0^* D)^{3/2} t^{3/2} \quad (5)$$

where z , F , K_n , N , D , M , ρ , C_0^* are, respectively, reacting electron number, Faraday constant, nucleation rate constant, maximum crystal nucleus density, diffusion coefficient of ion, atomic weight of electrodeposit, density of electrodeposit, and concentration of ion.

When the electrocrystallization process is instantaneous nucleation growth, the relation of I to t is represented by Eq.(6):

$$i = nFpN \left(\frac{M}{r} \right)^{1/2} (2C_0^* D)^{3/2} t^{1/2} \quad (6)$$

It is quite obvious that the electrocrystallization process of hafnium in the NaCl-KCl-NaF-HfO₂ system is an instantaneous hemispheroid three-dimensional nucleation process.

Conclusion

The electrochemical reaction mechanism and electrocrystallization process of hafnium in the NaCl-KCl-NaF-HfO₂ (xNaCl:xKCl:xNaF:xHfO₂=0.35:0.35:0.30:0.03) molten salt were studied at 973K. In this system, the reduction process of Hf⁴⁺ is a reversible process transferring 4 electrons in total and the product cannot be insoluble. Under the experimental conditions, the diffusion coefficient of hafnium ion in the system is $4.744 \times 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1}$. The electrocrystallization process of hafnium in the NaCl-KCl-NaF-HfO₂ system is an instantaneous hemispheroid three-dimensional nucleation process.

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